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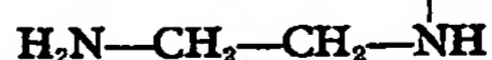
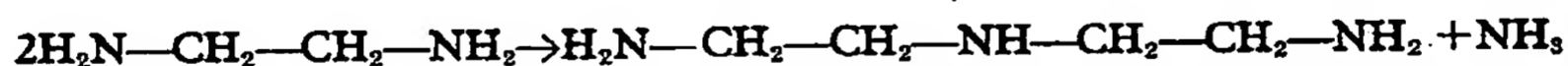
(54) MANUFACTURE OF DIETHYLENETRIAMINE AND TRIETHYLENETETRAMINE FROM ETHYLENEDIAMINE

(71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
Diethylenetriamine and triethylenetetramine, hereafter also abbreviated to DETA and TETA, have hitherto been manufactured by aminolysis of chloroethanes or hydroxyethanes.
For example, both compounds are produced, alongside one another, by the industrial-scale reaction of 1,2-dichloroethane with ammonia to give ethylenediamine. As the formation of ethylenediamine predominates, the desired products are dependent thereon and must be regarded as by-products.
A further halogen-exchange reaction is the reaction of 1,2-dichloroethane with ethylenediamine disclosed in U.S. Patent 3,462,493. A tabulation in this patent shows that under feasible reaction conditions either at least 20% of piperazinediethylenetriamine and 8.5% of piperazine, or 10% of piperazinediethylenetriamine and 17% of piperazine are produced. Accordingly, the proportion of more highly condensed amines produced always exceeds 27%.
A feature of both the above processes is the elimination of chlorine in the form of amine hydrochloride. The latter must be decomposed with strong alkali metal hydroxide solution, to give free amine and alkali metal chloride. The mixtures thus obtained contain amine, water, alkali metal hydroxide and

alkali metal chloride (e.g. salt). Working up by distillation is troublesome, because the alkali metal chloride contained in the solution progressively crystallizes out, and additional process steps are required. Furthermore, the disposal of the waste salt produced (the amount of which approximately corresponds to that of the amine produced) is expensive and detrimental to the environment.

An aminolysis reaction without objectionable salt formation is the reaction of ethylenediamine with ammonia in the presence of hydrogen over transition metal catalysts. The ethylenediamine produced is here again accompanied by numerous by-products, depending on the reaction conditions. They include some diethylenetriamine and triethylenetetramine, but also a large number of other products, e.g. aminoethylethanolamine, piperazine, aminoethyl-piperazine and viscous, high-boiling polyamines with varying numbers of hydroxyl groups. This applies particularly if reaction conditions are chosen under which DETA and TETA are produced in major amounts, as is desired. The separation of such mixtures is, however, always expensive and, as far as the high-boiling constituents are concerned, impossible.

Accordingly, the desired production of diethylenetriamine and triethylenetetramine by the aminolysis process described above has substantial disadvantages. These disadvantages show how important it would be to be able to manufacture DETA and TETA by condensation of ethylenediamine with elimination of ammonia, according to the equations:



In such a reaction, no water requiring subsequent separation from the amine would be produced. In view of the miscibility of

ethylenediamine and water and the existence of an azeotrope, this aspect is of great economic importance. Since the above reaction

also does not produce sodium chloride, simple working-up by distillation suffices. The ill-defined boiling ranges resulting from the presence of hydroxylic polyamines would not apply.

However, there has not previously been any indication that such a reaction is feasible. The reactions of this type hitherto disclosed only yield piperazine and piperazine homologs. Diethylenetriamine, assumed in the literature to be an intermediate in the formation of piperazine, has never previously been obtained from this reaction. Neither aminolysis of a hydrocarbon-OH bond nor amine condensation with elimination of ammonia have been disclosed as a method of arriving at triethylenetetramine.

We have now found that diethylenetriamine and/or triethylenetetramine may be manufactured by condensation of ethylenediamine with elimination of ammonia when the conversion of ethylenediamine is carried out over a catalyst containing at least one transition metal of group 8 of the Periodic Table of the Elements at from 100 to 150°C, preferably in the presence of hydrogen, the reaction being taken to a degree of conversion of 70% or less.

In the light of the above, the success of the process which has been found is surprising. The industrial importance of the new process over the previous methods of producing diethylenetriamine and triethylenetetramine, described above, is that it is simple to carry out and results in neither water of reaction, nor salts, nor reaction products of higher boiling point than triethylene tetramine. The desired products, namely diethylene triamine and triethylene tetramine, are obtained in a colorless and very pure form by distillation after having evaporated off the unconverted ethylenediamine.

We have found that only a narrow temperature range is suitable for carrying out the reaction. Above this temperature range piperazine is formed as the main product, whilst below this temperature range the rate of reaction in general greatly decreases. A particularly favorable reaction temperature for the formation of diethylene triamine and triethylenetetramine is from 110 to 130°C, substantially regardless of the choice of transition metal used in the catalyst. Furthermore, according to the invention, degrees of conversion of up to 70% are achieved at temperatures of from 100 to 150°C. Under these conditions the reaction product typically contains, on average up to 80% by weight of diethylene triamine, 12% by weight of triethylenetetramine and 8% by weight of piperazine, leaving out of account the unconverted ethylenediamine.

In general, a residence time of the ethylenediamine over the catalyst of up to 10

hours, preferably from 5 to 10 hours, is of value in achieving a good yield of the desired product, with longer residence times, piperazine is progressively produced with catalysts of average activity.

In addition to the temperature range to be used for the reaction, it is important that the concentration of catalyst should be high, e.g. 20% or more. The concentration is taken to be the filling ratio, i.e. the ratio of catalyst volume (measured as its bulk volume) to the effective (i.e. heated) volume of the reaction chamber, multiplied by the factor 100 if percentage data are required.

If the process is carried out with a suspended catalyst, mechanical mixing of the solid catalyst with the ethylene diamine and hydrogen is frequently necessary. In industrial operation, a very advantageous method is to pass the reactants continuously over a fixed bed catalyst located in a reaction tube, the reactants being at least partially liquid. However, in principle, the reaction can also be carried out in the gas phase, depending only on the pressure.

The catalysts may be supported on carriers or may be used unsupported. Preferably, supported catalysts are used in a fixed bed, whilst unsupported catalyst are preferred for the suspension process. However, the choice also depends on economic factors. Cobalt catalysts, for example, may also be used as unsupported catalysts in fixed beds.

Suitable catalysts are prepared forms of the transition metals of group 8 of the Periodic Table, including the noble metals. Auxiliary metals from other groups of the periodic system may also be present. Examples are catalysts containing copper and nickel, or copper, nickel and cobalt. In general, the following transition metals may be used: iron, nickel, cobalt, palladium, rhodium, ruthenium and platinum. They may be unsupported, or supported on carriers. In general they are in the form of the metal, at least in the active state. Noble metals, e.g. palladium, but also rhodium or platinum, if employed as salts, are converted to the metal under the reaction conditions and then become active for the purposes of the process. Isolation of the catalyst after the reaction may be facilitated if the catalyst has beforehand been supported on a carrier, e.g. active charcoal. Nickel and cobalt, when used as pure metals, are preferably employed in the skeletal form, i.e. as so-called Raney nickel or Raney cobalt. Catalysts of the above type have already been disclosed and are, e.g., used on a large scale in industry for reductive amination reactions. Instructions for the manufacture of suitable catalysts are to be found, e.g., in German Patent 1,172,268, U.S. Patent 2,225,059 and Org. Synth. 26, 77. A summarizing description may be found in Houben-Weyl, Methoden

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der organischen Chemie, 3rd edition, volume 4/2, page 137 et seq.

Surprisingly, the hydrogen pressure may be varied within wide limits. Under the predetermined temperatures, residence times and catalyst concentrations in question, hydrogen pressures of from atmospheric pressure to 250 bars are feasible and suitable. A suitable working range in practice, which give yields of, e.g., 80% of diethylenetriamine and 12% of triethylenetetramine, is, e.g., from 25 to 45 bars hydrogen pressure; under these conditions, a degree of conversion of, e.g., from 20 to 50%, in accordance with the invention, is achieved without difficulty.

The reaction products obtained from the reaction are suitably worked up by distillation. Unconverted ethylenediamine is obtained as the most volatile component and may be recycled to the process without having undergone additional purification. Accordingly, the process can be carried out particularly advantageously in a closed, continuous cycle, such as is shown diagrammatically in the accompanying drawing, including a reaction tube (3) with inlets for the reactants ethylenediamine (1) and hydrogen (2), a phase separator (4) for the reaction mixture and a distillation unit (5) for the liquid phase from the phase separator. The high-boiling products obtained, i.e. diethylenetriamine and triethylenetetramine, are taken as bottoms product (6) from the distillation unit (5). About the middle of the column (5), the piperazine also produced is taken off as a sidestream (7). The top product, ethylenediamine, which leaves as overhead product (8), is returned to the reactor (3) apart from a portion which is recycled to a distributor in the top of the distillation unit (5).

In the following Examples, which illustrate the invention, percentages are by weight.

EXAMPLE 1

A reaction tube of 30 mm diameter is filled with 700 ml of a catalyst which contains 4% of copper, 6% of cobalt and 8% of nickel on an aluminum oxide carrier. 100 ml/hour of ethylenediamine are passed continuously over the catalyst. The hydrogen pressure is 200 bars and the temperature 130°C. The material obtained is distilled without further treatment. 23% of the ethylene diamine employed is found to have been converted. The unconverted material is recycled to the reactor. Further distillation of the converted constituents gives 5% of piperazine, 7% of triethylenetetramine and 88% of colorless diethylenetriamine. The degree of purity of the diethylenetriamine is found, by gas chromatography, to be 99%. No higher-boiling by-products are formed in the reaction.

EXAMPLE 2

100 ml of ethylenediamine and 40 g of Raney nickel are left at 120°C under a hydrogen pressure of 1 bar in a moderately pressure-resistant reaction vessel. The reaction time is 8 hours. Analysis of the reaction product by gas chromatography shows that it contains 10% of diethylenetriamine and 2% of triethylenetetramine. Both products may be obtained in a purity of more than 98% by distillation.

EXAMPLE 3

Ethylene diamine in an amount of 100 ml/hour is passed over a copper-nickel catalyst. The temperature is 130°C, the prevailing hydrogen pressure 20 bars and the residence time is 6 hours. The reaction product contains 78% of diethylenetriamine, 15% of triethylenetetramine, 4% of aminoethylpiperazine and 3% of piperazine.

WHAT WE CLAIM IS:—

1. A process for the manufacture of diethylene triamine and/or triethylenetetramine by condensation of ethylenediamine with elimination of ammonia, wherein the conversion of ethylenediamine is carried out over a catalyst containing at least one transition metal of group 8 of the Periodic Table of the Elements at from 100 to 150°C, the reaction being taken to a degree of conversion of 70% or less.

2. A process as claimed in claim 1, wherein the reaction takes place in a reaction chamber in which the catalyst occupies at least 20% by volume of the available heated space.

3. A process as claimed in claim 1 or 2, carried out in the presence of hydrogen.

4. A process as claimed in any of claims 1 to 3, carried out at a temperature of from 110 to 130°C.

5. A process as claimed in any of claims 1 to 4, wherein the residence time of the ethylene diamine over the catalyst is up to 10 hours.

6. A process as claimed in any of claims 1 to 5, wherein the reactants are at least partly liquid and are passed continuously over a fixed bed catalyst located in a reaction tube.

7. A process as claimed in any of claims 1 to 6, wherein a nickel, cobalt, palladium, ruthenium or platinum catalyst is used.

8. A process as claimed in claim 7, wherein cobalt catalyst or copper-nickel catalyst is used.

9. A process as claimed in claim 3 or in any of claims 4 to 8 as appendent to claim 3, wherein a hydrogen pressure of from 25 to 45 bars is used.

10. A process for the manufacture of di-

ethylenetriamine and/or triethylenetetramine carried out substantially as described in any of the foregoing Examples.

- 5 11. Diethylenetriamine and triethylene-tetramine when manufactured by a process as claimed in any of claims 1 to 10.

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

